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Electrocatalytic oxidation of methanol at tantalum oxide-modified Pt electrodes

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HIGHLIGHTS

► TaOx-modified Pt electrode was prepared by electrodeposition of Ta oxide on Pt substrate in room temperature ionic liquid.
► TaOx-modified Pt electrode shows an enhanced electrocatalytic activity towards the oxidation of methanol.
► The observed electrocatalysis originates from the metal–metal oxide d–d electronic interaction and the OH spillover.

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ABSTRACT

The current study addresses the electrocatalytic activity of tantalum oxide (TaOx)-modified Pt electrode as a novel catalyst for methanol oxidation in acidic media. The modified Pt electrode is shown to support a larger oxidation current of methanol compared to that obtained at the unmodified Pt electrode concurrently with a favorable significant shift of the onset potential of methanol oxidation. Tafel plots, with a slope close to 0.118 V decade^{-1}, were obtained for methanol oxidation at the unmodified and TaOx-modified Pt electrodes, reflecting that the methanol oxidation proceeds with the first electron transfer as the rate-determining step. The observed enhancement was attributed to a favorable d–d metal–metal oxide interaction which changes the electronic property of Pt and hence enhances the oxidation of the adsorbed reaction intermediates (e.g., CO_{ads}). Moreover, a possible contribution of the OH spillover via a so-called "bifunctional mechanism" is proposed. The influence of the temperature on the oxidation current of methanol at the TaOx-modified Pt electrode is investigated and apparent activation energy, E_a, for methanol oxidation is calculated as 39 kJ mol^{-1} at a specific potential. The proposed catalyst showed a good enhancement for methanol oxidation for a prolonged time of continuous potentiostatic electrolysis.

1. Introduction

Fuel cells have been projected as promising energy devices responding to the world's increasing demand of safe, eco-friendly and noiseless energy sources [1–3]. In this context, direct alcohol fuel cells, employing, e.g., methanol as a fuel, have received a considerable attention [4] in view of its virtues, e.g., high solubility in aqueous electrolytes, easy handling, transport and storage in comparison with hydrogen gas as a fuel. Moreover, methanol has a high theoretical density of energy (6 kWh kg^{-1}) which is comparable to that of gasoline (10–11 kWh kg^{-1}) [5–8].

The electrooxidation of methanol at the Pt electrode is a complex reaction which brings about the formation of a variety of adsorbed intermediates and/or poisons such as CO [5,9–15], which blocks the active Pt sites and thus causes a significant deterioration of its catalytic activity. This renders the unmodified Pt electrode incapable of oxidizing methanol at a satisfactory rate at a sufficiently low potential. In this context, several modifications of the Pt electrode have been reported in order to mitigate such a poisoning effect aiming at the enhancement of methanol oxidation by increasing the anode tolerance against the reaction intermediates (particularly the poisoning adsorbed CO). These include alloying Pt with another metal such as Rh [5], Ru [16], Sn [17], Mo [18] or Au [19]. Moreover, Pt electrodes modified with metal oxide (e.g., MoO_3, TiO_2, CeO_2, SnO_2 or Nb_2O_5) have been reported as possible anodes for methanol and CO oxidation reactions [20–26], in which the

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activity of the modified Pt catalyst towards methanol oxidation is significantly improved. Consistently, we have reported the enhanced electrooxidation of formic acid [27] and formaldehyde [28] at TaOx-modified Pt electrodes. The observed enhancement has been explained in view of the so-called "bifunctional mechanism", in addition to the favorable electronic interaction between TaOx and the underlying Pt electrode. Thus, in view of their virtues and in continuation of our investigations of the versatile catalytic activity of the Pt–TaOx binary catalysts [27–33], the current study aims at the investigation of their electrocatalytic activity towards methanol oxidation in acidic media. Cyclic voltammetry (CV) and chronoamperometry techniques are used in this study. The influence of various electrolysis parameters on the electrooxidation of methanol (e.g., supporting electrolyte temperature as well as the potential scan limit in the anodic direction) has been investigated and optimized. The proposed catalyst showed a good enhancement for methanol oxidation for a prolonged time of a continuous potentiostatic electrolysis.

2. Experimental

2.1. Materials

Reagents of analytical grade (purchased from Kanto Co. and Wako Pure Co., Japan) were used as received without further purification. All the solutions were prepared by appropriate dilution with Milli-Q (18.2 MΩ cm) deionized water.

2.2. Preparation of TaOx-modified Pt electrode

A one side of a Pt plate covered with a Teflon tape (leaving an exposed geometric area of 6.0 mm^2) was used as the working electrode. The modification of the Pt electrode with TaOx was performed in two steps: First, Ta metal was electrodeposited on the Pt electrode by a controlled-potential electrolysis at −2.2 V (vs. Pt) for 100 s in the ionic liquid, 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl) imide, containing 0.2 M TaF_5 and 0.2 M LiF at 100 °C [34]. The Ta-modified Pt electrode was successively washed with acetone, ethanol and hot 2-propanol. Second, the Ta-modified Pt electrode was calcinated at 600 °C in an electric furnace for 30 min under air atmosphere to prepare TaOx-modified Pt electrode.

2.3. Electrochemical measurements

Electrochemical measurements were performed in a conventional three-electrode glass cell using an ALS/Chi 750B electrochemical analyzer (BAS Co., Ltd.). An Ag|AgCl|KCl(sat.) and a spiral platinum wire were used as the reference and the counter electrodes, respectively. All the electrochemical measurements were performed under inert gas atmosphere (i.e., N_2 or Ar) at room temperature (25 ± 1 °C). All the current densities were calculated on the basis of the geometric surface area of the Pt electrode.

2.4. Surface analysis of modified electrodes

XPS measurements of the TaOx-modified Pt electrodes were performed by ESCA-3400 electron spectrometer (SHIMADZU) using an unmonochromatized X-ray source (Mg Kα ($h\nu$ = 1253.6 eV) anode, emission current: 20 mA, and acceleration voltage: 10 kV). The SEM image of the modified electrode surfaces was obtained using a field emission scanning electron microscope S5200 (HITACHI, Japan) at an acceleration voltage of 10 kV and a working distance of 4–5 mm.

3. Results and discussion

3.1. Characterization of TaOx-modified Pt electrode

Fig. 1 shows a typical SEM image of the TaOx-modified Pt electrode. This figure shows that the electrodeposited tantalum oxide homogeneously covers the Pt electrode surface in a rather porous texture which allows the easy access of the solution species to the underlying Pt surface.

Analysis of our recent XPS data of the thus-prepared TaOx-modified Pt electrodes [27,28] has revealed that Ta^{5+} is the predominant species on the Pt surface, i.e., tantalum oxide (TaOx) exists as the stoichiometric Ta_2O_5. Further analysis of the deposited TaOx layer has been performed in the current study. That is, a controlled erosion of the top layer of Ta_2O_5 was performed via Ar^+ etching and then the XPS spectrum was measured (Fig. 2). Upon deconvolution of the spectrum, several new peaks were obtained with binding energies which correspond to Ta cations with lower oxidation states than 5+ (i.e., Ta^{z+} with $z < 5$), but are still higher than that reported for elemental Ta. This indicates the existence of non-stoichiometric tantalum oxides (i.e., TaOx) beneath the surface monolayer of the stoichiometric Ta_2O_5. Furthermore, a positive shift of the Pt $4f_{7/2}$ binding energy was observed for the TaOx-modified Pt electrode (data are shown elsewhere [27]) compared with that reported for elemental Pt, reflecting a strong electronic interaction between TaOx and the underlying Pt substrate.

The electrochemical characterization of the TaOx–Pt electrode has been performed by measuring the CV response in N_2–saturated 0.1 M H_2SO_4 as shown in Fig. 3. Two couples of well-defined peaks corresponding to a hydrogen adsorption–desorption were observed at the TaOx-modified Pt (curve b) electrode with a larger current compared to that obtained at the unmodified Pt electrode (curve a). This enhancement of the hydrogen adsorption–desorption response at the modified electrode, albeit with a lower accessible surface area of Pt compared with the unmodified Pt electrode, is explained in view of a so-called hydrogen spillover–reverse spillover mechanism [30]. Interestingly, the current for the formation of the Pt oxide layer and its reduction was also found larger at the TaOx-modified Pt electrode than that obtained at the unmodified Pt electrode, which is attributed to OH spillover at the TaOx-modified Pt electrode [35]. This observation provides a direct evidence for the high affinity of the TaOx-modified Pt electrode towards OH species and the essential role of tantalum oxide in this behavior (c.f. Sec. 3.7).

The estimation of the surface coverage of TaOx (θ) on the Pt electrode has been carried out by measuring CVs for the

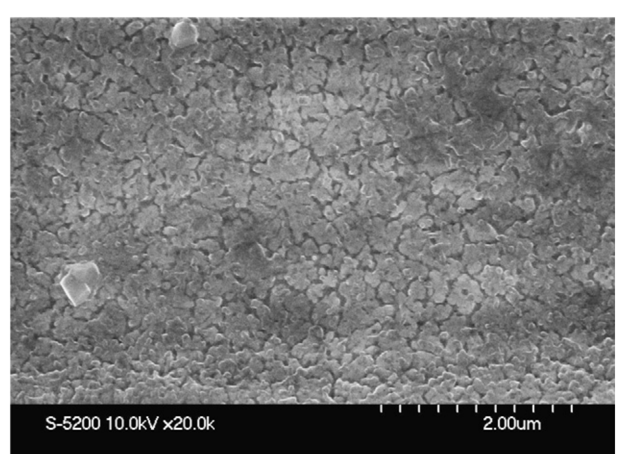


Fig. 1. SEM image of TaOx-modified Pt electrocatalyst.

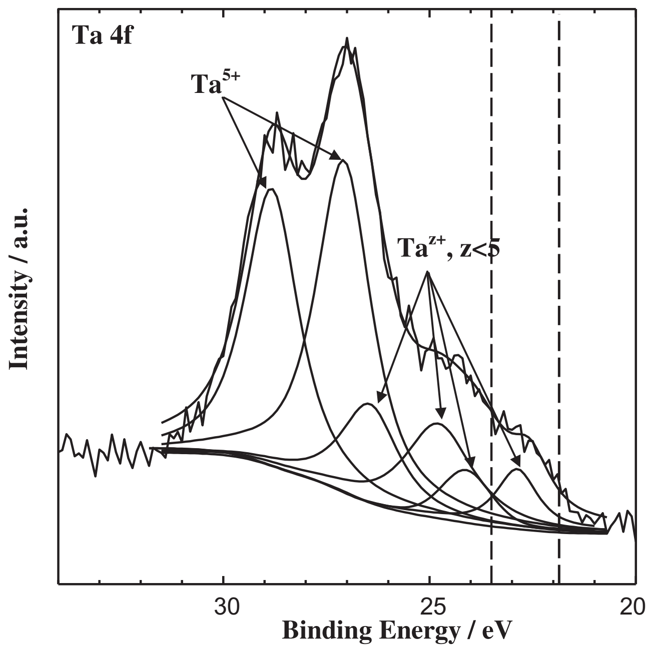


Fig. 2. Ta (4f) XPS spectra of TaOx-modified Pt electrode after Ar^+ etching for 1 min to observe the chemical states of Ta under the surface of Ta_2O_5 layer. The dotted lines correspond to the binding energies of $4f_{7/2}$ and $4f_{5/2}$ of elemental Ta.

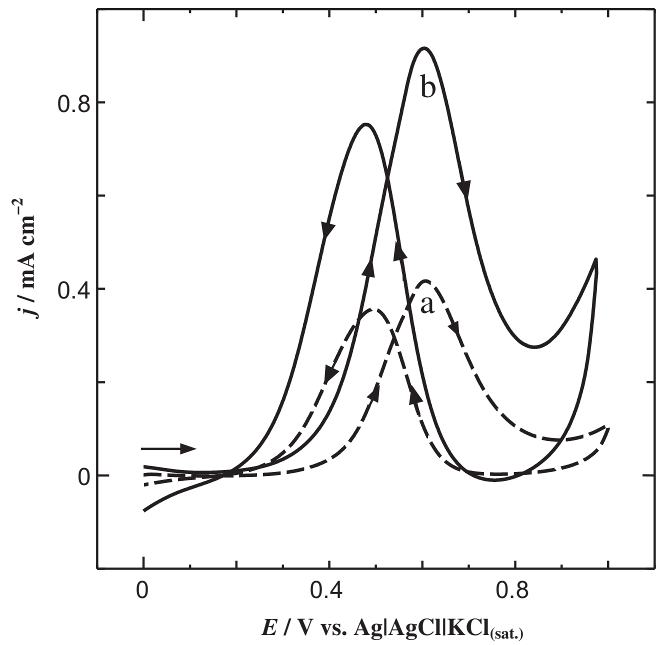


Fig. 4. CVs obtained at (a) bare Pt and (b) TaOx-modified Pt electrodes in Ar-saturated 0.5 M H_2SO_4 solution containing 0.1 M CH_3OH. Potential scan rate: 50 mV s^{-1}.

$[Fe(CN)_6]^{4-}/[Fe(CN)_6]^{3-}$ redox couple at the unmodified and TaOx-modified Pt electrodes in 0.1 M KNO_3 solution. A comparison between the peak currents for the redox species at the unmodified and modified Pt electrodes resulted in a value of θ of 0.3 [27].

3.2. Methanol electrooxidation

The thus-fabricated TaOx-modified Pt electrode was tested for its catalytic activity towards methanol oxidation. Fig. 4 shows the CVs measured at (a) unmodified and (b) TaOx-modified Pt ($\theta = 0.3$) electrodes in a deaerated 0.5 M H_2SO_4 containing 0.1 M methanol. Inspection of this figure reveals the appearance of an anodic peak (j^a_{pf}) at ca. 0.6 V vs. Ag|AgCl|KCl(sat.) at the unmodified Pt electrode, during the forward potential scan (curve a). The gradual decrease of current, at potentials >ca. 0.6 V coincides with the onset of Pt oxide formation (see Fig. 3) which decreases the number of Pt active sites available for the methanol oxidation. The appearance of another anodic peak (j^a_{pb}), during the backward scan, was assigned to the oxidation of methanol and/or methanol residues (e.g., CO) [36,37]. Interestingly, the modification of the Pt electrode with TaOx greatly improves its catalytic activity towards methanol oxidation (curve b). That is, the onset potential of methanol oxidation shifts by ca. 0.15 V to the negative direction of potential compared to that observed at the unmodified Pt electrode concurrently with a two-fold increase in j^a_{pf}. This catalytic enhancement points to a crucial role of TaOx in the oxidation of methanol.

Another important index of the catalytic enhancement is the ratio between j^a_{pf} and j^a_{pb} (i.e., j^a_{pf}/j^a_{pb}). This ratio has been often used to describe the catalyst tolerance of the anodes against the incompletely oxidized species which are accumulated on their surfaces [38,39]. A large ratio means good tolerance of the anode against the poisoning species, i.e., more effective removal of the poisoning species on the electrode surface during the forward potential scan. In the current study, the j^a_{pf}/j^a_{pb} ratios obtained at the TaOx-modified and unmodified Pt electrodes are 1.24 and 1.12, respectively, indicating that the TaOx-modified Pt catalyst has a better tolerance than the unmodified Pt electrode.

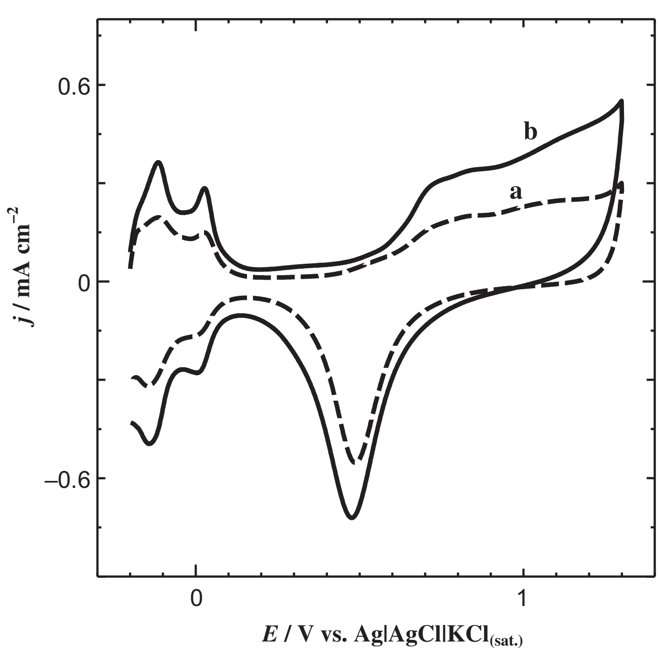


Fig. 3. Characteristic cyclic voltammograms (CVs) measured at (a) bare Pt electrode and (b) TaOx-modified Pt electrode in N_2-saturated 0.1 M H_2SO_4 solution. Potential scan rate: 75 mV s^{-1}.

3.3. Tafel plots

Further examination of the catalytic performance of the TaOx-modified Pt electrode towards methanol oxidation has been carried out by measuring the Tafel plots based on the equation given below [40].

$$E = E_{eq} + \frac{2.3RT}{(1-\alpha)nF}\log i_o - \frac{2.3RT}{(1-\alpha)nF}\log i \quad (1)$$

where E is the electrode potential, E_{eq} is the equilibrium potential, i_o is the exchange current density and the other symbols have their usual meanings. Fig. 5 shows Tafel plots for methanol oxidation at the (a) unmodified and (b) TaOx-modified Pt electrodes obtained in 0.5 M H_2SO_4 solution containing 0.1 M methanol. Tafel slopes of 0.121 and 0.104 V decade^{-1} for the former and the latter electrodes, respectively, being close to the normal Tafel slope of 0.118 V decade^{-1}. This means that methanol oxidation proceeds at the unmodified and the modified Pt electrodes via the same rate-determining step which is frequently assigned to be the unit reaction involving the first electron transfer [41], i.e., a splitting of the first C–H bond of CH_3OH molecule (see Eq. (2)).

$$Pt + CH_3OH \rightarrow Pt(H-CH_2OH)_{ad} \longrightarrow Pt(CH_2OH)_{ad} + H^+ + e \quad (2)$$

The slightly smaller Tafel slope obtained at the modified electrode indicates a more facile electrooxidation of methanol at the TaOx-modified Pt surface than at the unmodified Pt surface [42].

3.4. Current transients

In order to evaluate the long term catalytic performance of the TaOx-modified Pt electrode for methanol oxidation, current transients (j–t) were measured at 0.5 V vs. Ag|AgCl|KCl(sat.) at (a) unmodified and (b) TaOx-modified Pt electrodes in 0.5 M H_2SO_4 solution containing 0.1 M methanol (Fig. 6). At this potential (0.5 V), tenacious reaction intermediates such as CO_{ad} would begin to accumulate on the catalyst surface due to the continuous oxidation of methanol. A significantly larger oxidation current is obtained for the oxidation of methanol at the TaOx-modified Pt electrode over the entire period of electrolysis compared to that obtained at the unmodified Pt electrode. Moreover, the oxidation current obtained at the unmodified Pt electrode is completely ceased after about 300 s of continuous electrolysis. These demonstrate the relative long term-stability and the preferential oxidation of methanol at the modified electrode and its high tolerance against the reaction intermediates.

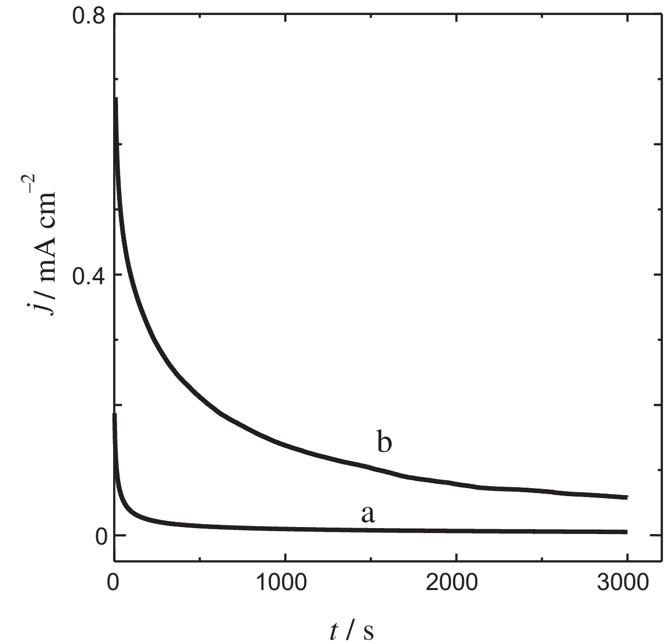


Fig. 6. Current transients (j–t) curves obtained at (a) bare Pt and (b) TaOx-modified Pt electrodes in 0.5 M H_2SO_4 solution containing 0.1 M methanol at 0.5 V.

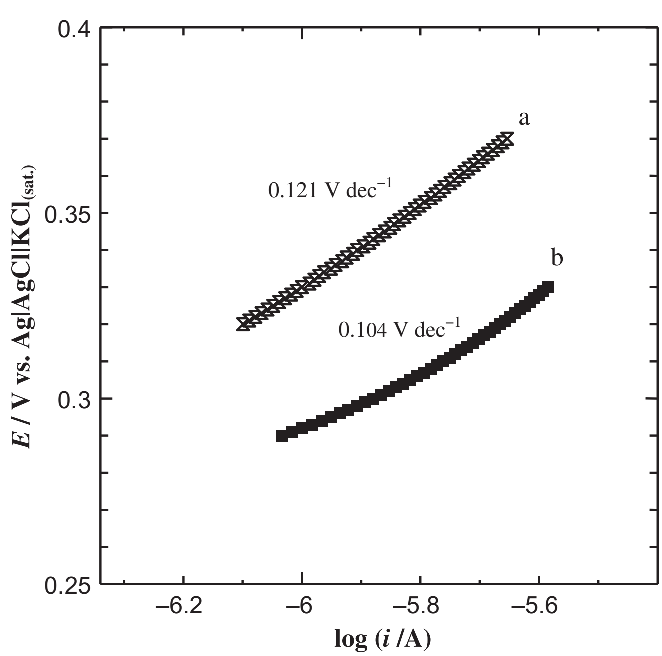


Fig. 5. Tafel plots obtained at (a) bare Pt and (b) TaOx-modified Pt electrodes for the methanol electrooxidation. Data were taken from Fig. 4.

3.5. Influence of temperature

The solution temperature is another vital parameter in determining the catalytic performance of the proposed TaOx-modified Pt electrode. A typical set of CVs for the methanol oxidation at the TaOx-modified Pt electrode were obtained at various solution temperatures (25–60 °C) and are shown in Fig. 7. This figure shows an increase of j^a_{pf} and j^a_{pb} with temperature up to 60 °C (see inset of Fig. 7). Note that a possible evaporation of methanol might occur at temperatures higher than its boiling point (64.5 °C). This might lead to a significant change in methanol concentration and consequently an error in the measured CV response for its oxidation. An increase in j^a_{pf} and j^a_{pb} with temperature reflects a more favorable kinetics of the methanol oxidation at both potential scan directions. The value of an apparent activation energy (E_a) is calculated by plotting the current (I) at a specific potential as a function of temperature (T in K) according to Arrhenius equation. Fig. 8 shows a representative Arrhenius plot for the oxidation of 0.1 M methanol in 0.5 M H_2SO_4 in which log I is plotted against T^{-1} at a potential of 0.64 V and the linear plot gives 39 kJ mol^{-1} as E_a. Similar values, 20–70 kJ mol^{-1}, have been reported for the methanol oxidation at Pt-supported electrodes in acidic media [43–45] (Fig. 8).

3.6. Effect of potential scan limit

Fig. 9 shows CVs for the methanol oxidation in 0.5 M H_2SO_4 containing 0.1 M methanol at the TaOx-modified Pt electrode in which the forward potential scan limit is varied in the range of 0.8–1.2 V. It is obvious that extending the potential limit to the more positive direction does not affect the peak potential or the peak current of methanol oxidation obtained during the forward potential scan. On the other hand, the anodic peak current (j^a_{pb}) and potential (E^a_{pb}), obtained during the backward potential scan, are very much affected by the value of positive-going potential limit. That is, a monotonic decrease in j^a_{pb} is observed together with

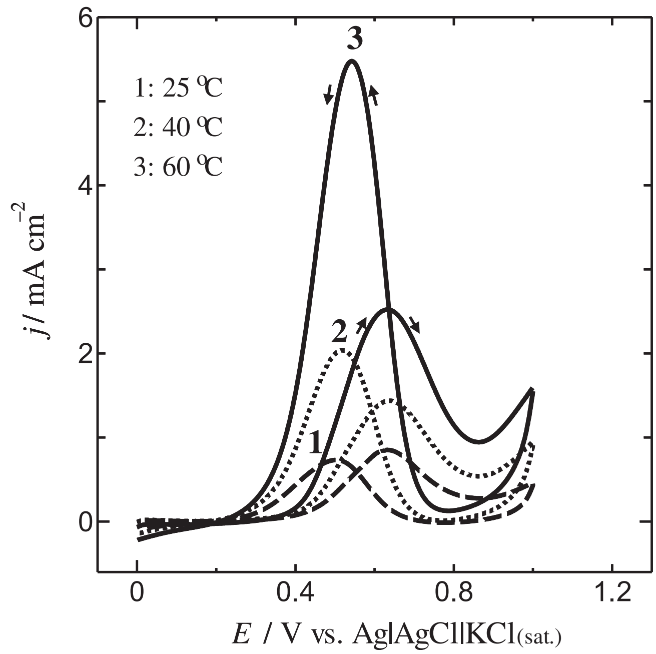


Fig. 7. CVs obtained at TaOx-modified Pt electrode in Ar-saturated 0.5 M H_2SO_4 containing 0.1 M methanol at different temperatures. Potential scan rate: 50 mV s^{-1}. Inset shows the variation of the anodic peak currents (a) j^a_{pf} and (b) j^a_{pb} with temperature.

a negative shift of E^a_{pb}, upon extending the potential limit from 0.8 to 1.2 V vs. Ag|AgCl|KCl(sat.). This is attributed to the gradual increase of the amount of Pt oxide on the catalyst surface which is undesired for the oxidation of methanol and/or methanol residue during the negative going potential excursion [46,47]. That is, during the negative going potential scan, the oxidation reaction is controlled by the amount of Pt oxide on the catalyst surface. The reduction of the Pt oxide layer (proceeds with a slow kinetics) is a pre-requisite for the observation of the anodic peak, during the reverse scan.

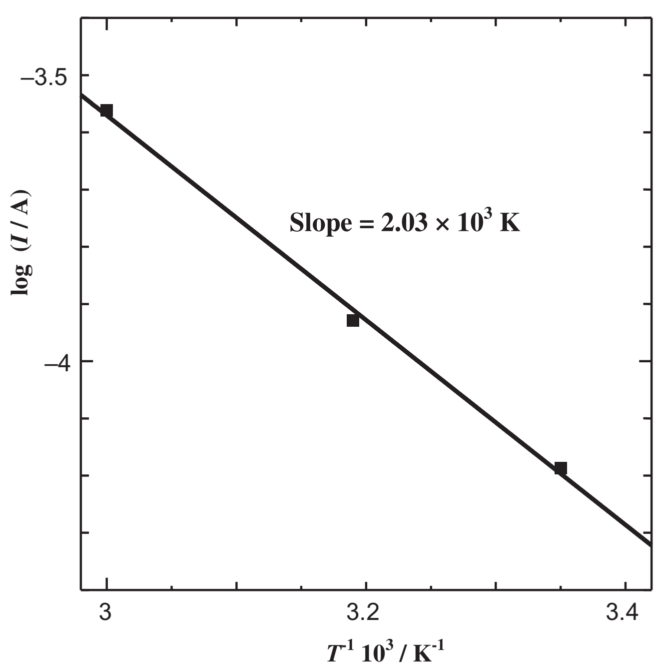


Fig. 8. Variation of the logarithm of the peak current (log I) with the inverse of absolute temperature (T^{-1}). Data were taken from Fig. 7.

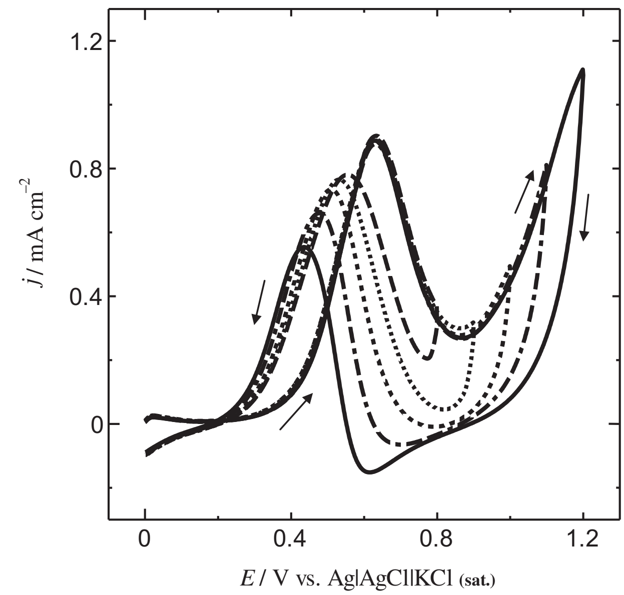


Fig. 9. CVs obtained at TaOx-modified Pt electrode in Ar-saturated 0.5 M H_2SO_4 containing 0.1 M methanol at 50 mV s^{-1} for different forward scan limits.

3.7. Role of TaOx

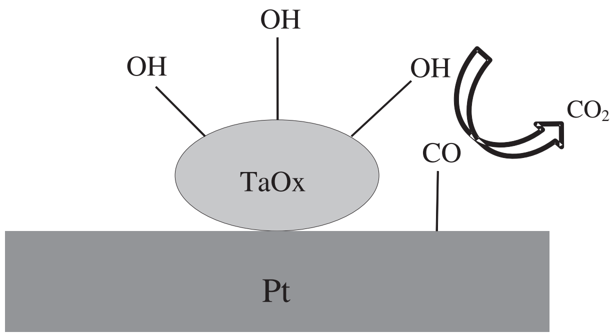
The significant enhancement of methanol oxidation at the TaOx-modified Pt electrode points to a crucial role of TaOx in the process. This might originate from one or a combination of the following reasons:

1- The d–d metal–metal oxide interaction between Pt and TaOx, which results in the electron donation from Pt to TaOx, i.e., induces a positive charge on the Pt surface, weakens the Pt–CO_{ad} bond strength [48], enhances its oxidative removal and decreases its surface coverage on the Pt surface. A similar explanation is given by Justin et al. [25] for the electrooxidation of methanol at Pt–Nb_2O_5/C.

2- The high affinity of the TaOx-modified Pt electrode towards OH species (see Fig. 3) would assist the methanol oxidation by providing oxygen species at the catalyst surface at lower potential compared to the unmodified Pt electrode. This high affinity might originate from the existence of the non-stoichiometric tantalum oxide (TaOx) with some oxygen vacancies in its lattice (see Fig. 2) which may accelerate the dissociation of H_2O molecules to form OH_{ads} (Eq. (3)), thus facilitating the oxidation of methanol and/or adsorbed poisons (e.g., CO) (Eq. (4)) and thus retrieves the Pt active sites for the methanol oxidation reaction to proceed continuously. Scheme 1 provides a plausible illustration of a so-called bifunctional mechanism [49,50]. Similar mechanism has been reported for the enhanced electrooxidation of CO_{ads} by ternary catalysts of PtRuMo/C [51], in which Mo enriched the surface of the catalyst with adsorbed OH (MoOx–OH_{ads}) at low potentials resulting in an improved methanol oxidation. Alternatively, one might assign the high affinity of the modified Pt electrode towards OH species (Fig. 3) to the OH spillover phenomenon [27,28,35] in which OH adsorbed on the Pt surface is spilled over to the TaOx.

$$\text{TaOx} + H_2O \rightarrow \text{TaOx-OH}_{ads} + H^+ + e^- \quad (3)$$

$$\text{TaOx-OH}_{ads} + \text{Pt-CO}_{ads} \rightarrow \text{Pt} + \text{TaOx} + CO_2 + H^+ + e^- \quad (4)$$



Scheme 1. The bifunctional mechanism of TaOx-modified Pt catalyst for enhancing CO electrooxidation.

4. Conclusions

TaOx-modified Pt electrode shows a significantly enhanced catalytic activity towards the oxidation of methanol in sulfuric acid. Tafel plots, with a slope close to 0.118 V decade^{-1}, were obtained for methanol oxidation at the unmodified and Ta_2O_5-modified Pt electrodes, reflecting that the methanol oxidation proceeds with the first electron transfer as the rate-determining step. The observed enhancement is explained in view of the favorable d–d metal–metal oxide interaction which changes the electronic property of Pt together with the enrichment of the catalyst surface with OH species and consequently the oxidation of the adsorbed reaction intermediates (e.g., CO) to CO_2 via a so-called bifunctional mechanism. The influence of some operating parameters (including temperature as well as positive potential scan limit) on the catalytic activity of TaOx-modified electrode towards methanol oxidation is investigated, discussed and optimized.

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References

[1] K.V. Kordesh, G.R. Simader, Chem. Rev. 95 (1995) 191.
[2] O. Diat, G. Gebel, Nat. Mater. 7 (2008) 13.
[3] K. Asazawa, K. Yamada, H. Tanaka, A. Oka, M. Taniguchi, T. Kobayashi, Angew. Chem. Int. Ed. 46 (2007) 8024.
[4] R.F. Service, Science 296 (2002) 1222.
[5] W. Tokarz, H. Siwek, P. Piela, A. Czerwinski, Electrochim. Acta 52 (2007) 5565.
[6] C. Lamy, A. Lima, V. LeRehun, F. Delime, C. Countanceau, J. Leger, J. Power Sources 105 (2002) 283.
[7] A.S. Arico, S. Srinivasan, V. Antonucci, Fuel Cells 1 (2001) 133.
[8] P. Piela, P. Zelenay, Fuel Cell Rev. 1 (2004) 17.
[9] N.R. Elezovic, B.M. Babic, V.R. Radmilovic, S.Lj. Gojkovic, N.V. Krstajic, Lj.M. Vracar, J. Power Sources 175 (2008) 250.
[10] L. Niu, Q. Li, F. Wei, S. Wu, P. Liu, X. Cao, J. Electroanal. Chem. 578 (2005) 331.
[11] F. Vigier, F. Gloaguen, J.M. Léger, C. Lamy, Electrochim. Acta 46 (2001) 4331.
[12] M.H. Pournaghi-Azar, B. Habibi, J. Electroanal. Chem. 601 (2007) 53.
[13] T. Iwasita, Electrochim. Acta 47 (2002) 3663.
[14] A. Cuesta, J. Am. Chem. Soc. 128 (2006) 13332.
[15] T.D. Jarvi, S. Sriramulu, E.M. Stuve, J. Phys. Chem. B 101 (1997) 3649.
[16] T. Sato, K. Kunimatsu, M. Watanabe, H. Uchida, J. Nanosci. Nanotechnol. 11 (2011) 5123.
[17] D.M. Han, Z.P. Guo, R. Zeng, C. Kim, Y.Z. Meng, H.K. Liu, Int. J. Hydrogen Energy 34 (2009) 2426.
[18] S. Mukerjee, R.C. Urian, Electrochim. Acta 47 (2002) 3219.
[19] Y.Q. Wang, Z.D. Wei, L. Li, M.B. Ji, Y. Xu, P.K. Shen, J. Phys. Chem. C 112 (2008) 18672.
[20] P. Justin, G.R. Rao, Int. J. Hydrogen Energy 36 (2011) 5875.
[21] P. Justin, G.R. Rao, Catal. Today 141 (2009) 138.
[22] Y. Zhou, Y. Gao, Y. Liu, J. Liu, J. Power Sources 195 (2010) 1605.
[23] S. Yoo, T. Jeon, K. Lee, K. Park, Y. Sung, Chem. Commun. 46 (2010) 794.
[24] M. Saha, R. Li, M. Cai, X. Sun, Electrochem. Solid-State Lett. 10 (2007) B130.
[25] P. Justin, P.H.K. Charan, G.R. Rao, Appl. Catal. B: Environ. 100 (2010) 510.
[26] A. Ueda, Y. Yamada, T. Ioroi, N. Fujiwara, K. Yasuda, Y. Miyazaki, T. Kobayashi, Catal. Today 84 (2003) 223.
[27] J. Masud, M.T. Alam, M.R. Miah, T. Okajima, T. Ohsaka, Electrochem. Commun. 13 (2011) 86.
[28] J. Masud, M.T. Alam, T. Okajima, T. Ohsaka, Chem. Lett. 40 (2011) 252.
[29] Z. Awaludin, M. Suzuki, J. Masud, T. Okajima, T. Ohsaka, J. Phys. Chem. C 115 (2011) 25557.
[30] S. Sata, M.I. Awad, M.S. El-Deab, T. Okajima, T. Ohsaka, Electrochim. Acta 55 (2010) 3528.
[31] M.I. Awad, S. Sata, K. Kaneda, M. Ikematsu, T. Okajima, T. Ohsaka, Electrochem. Commun. 8 (2006) 1263.
[32] K. Kitsuka, K. Kaneda, M. Ikematsu, M. Iseki, K. Mushiake, A.M. Mohammad, T. Ohsaka, Chem. Lett. 36 (2007) 806.
[33] M.S. El-Deab, M.I. Awad, T. Ohsaka, Electrocatalytic applications of manganese oxide, tantalum oxide and titanium oxide nanostructures-modified electrodes, in: A. Umar, Y.-B. Hahn (Eds.), Metal Oxide Nanostructures and Their Applications, vol. 3, American Scientific Publishers, California, 2010 (Chapter 10).
[34] S.Z. El Abedin, H.K. Farag, E.M. Moustafa, U. Welz-Biermann, F. Endres, Phys. Chem. Chem. Phys. 7 (2005) 2333.
[35] I. Boskovic, S.V. Mentus, J.M. Pjescic, Electrochem. Commun. 7 (2005) 797.
[36] W.S. Li, L.P. Tian, Q.M. Huang, H. Li, H.Y. Chen, X.P. Lian, J. Power Sources 104 (2002) 281.
[37] R. Manohara, J.B. Goodenough, J. Mater. Chem. 2 (1992) 875.
[38] H. Gao, S. Liao, J. Zeng, Y. Xie, J. Power Sources 196 (2011) 54.
[39] Z. Liu, X.Y. Ling, X. Su, J.Y. Lee, J. Phys. Chem. B 108 (2004) 8234.
[40] A.J. Bard, L.R. Faulkner, Electrochemical Methods; Fundamentals and Applications, John Wiley & Sons, Inc., New York, 1980 (Chapter 3).
[41] M. Umeda, H. Sugii, I. Uchida, J. Power Sources 179 (2008) 489.
[42] H.B. Hassan, J. Fuel Chem. Technol. 37 (2009) 346.
[43] A.V. Palenzuela, F. Centellas, J.A. Garrido, C. Arias, R.M. Rodriguez, E. Brillas, P.L. Cabot, J. Power Sources 196 (2011) 3503.
[44] S.L. Gojkovic, T.R. Vidakovic, D.R. Durovic, Electrochem. Acta 48 (2003) 3607.
[45] H. Gharibi, K. Kakaei, M. Zhiani, M.M. Taghiabadi, Int. J. Hydrogen Energy 36 (2011) 13301.
[46] M.H. Pournaghi-Azar, B. Habibi, J. Electroanal. Chem. 605 (2007) 136.
[47] A.N. Golikand, M. Ghannadi Maragheh, S. Sedaghat Sherehjini, K.M. Taghi-Ganji, M. Yari, Electroanalysis 18 (2006) 911.
[48] Z. Wang, G. Yin, Y. Lin, J. Power Sources 170 (2007) 242.
[49] D.H. Lim, D.H. Choi, W.D. Lee, H.I. Lee, Appl. Catal. B: Environ. 89 (2009) 484.
[50] M. Watanabe, S. Motoo, J. Electroanal. Chem. 60 (1975) 275.
[51] N. Tsiouvaras, M.V. Martinez-Huerta, O. Paschos, U. Stimming, J.L.G. Fierro, M.A. Pena, Int. J. Hydrogen Energy 35 (2010) 11478.